Indian J. Phys. **49**, 928–938 (1975)

Energy of formation of Schottky defects in alkali halides.

S. Chaudhuri, D Roy and A. K. Ghosh

Department of General Physics and X-rays,
Indian Association for the Cultivations of Science, Calcutta 700 032

(*Received* 10 *March* 1975)

The energies of formation of Schottky pairs, E_{SD}, in NaCl, NaBr, NaI, KF, KCl, KBr, KI, RbCl, RbBr and RbI have been calculated by utilizing a *point polarisable ion model* as well as a *negative ion polarizable shell model* Van der Waals and three-body interactions have been considered. Point polarizable ion model shows a better agreement with the experiments than the shell model. The probable reasons have been discussed, and a new possible method of finding shell model parameters has been put forward The three-body forces have been found seemingly not to contribute very much towards E_{SD}.

1. Introduction

The success of Born model of cohesion has encouraged many workers in the past (Mott & Littleton 1938, Bassani & Fumi 1954, Kurosawa 1948, Scholz 1968) to develop atomistic calculation of formation and migration energies of simple point defects, like Schottky pairs, in alkali halides. Most of these calculations have been devoted to improve the original work of Mott and Littleton (hereinafter referred to as ML) in one way or another The ML approach, in essence, is to divide the crystal into two regions (I and II) around the defect. Exact lattice calculations are performed for the region I while region II is treated via the continuum theory.

Bassani & Fumi (1954) included next nearest neighbours in the Born-Mayer repulsion between the ions in region I; Scholz (1968) extended the region I to more distant ions and Kurosawa (1958) minimised the energy (considered in a more generalized manner) of the relaxed lattice with respect to the displacements and dipole moments to find out the relaxation of the ions in region I Brauer (1952) was the first to contemplate that since the relaxation of the lattice in region II is figured out through the continuum properties, it is necessary so consider an elastic displacement of the ions over and above their displacements originating from electrostatic reasons. Boswarva & Lidiard (1967) (hereinafter referred to as BL) recently found out that the elastic displacement in the scheme of Brauer over-emphasizes the displacements of the distant ions, and so they (BL) have suggested a new scheme which takes care of that Moreover, BL included the so-called van der Waals (Margenau 1939) terms in their calculations.

A completely different approach to the problem of finding outs the lattice relaxation around point defects and hence-finding out their energy of formation has been offered by Hardy & Lidiard (1967) and Karo & Hardy (1971). This approach is essentially an extension of the method of Kuaki (1957) to the case of charged defects

One common feature in most of these calculations is that different workers have utilized a point polarizable ion model for the calculations The dipole moment of the nearest neighbours ν, is a parameter in the calculations, while those of the distant neighbours are approximated through the continuum theory ν is then found out in a self-consistent manner from the force-balance (or energy minimization) procedure Different versions of shell model (SM) (Woods *et al* 1960, Bick & Overhauser 1958), very often used in lattice dynamics, however, offer a picture for the mechanism of the polarization of ions Therefore, it is interesting to examine the formation energy of Schottky defects by an appeal to the SM The extension of this model to all neighbours is cumbersome and not much meaningful from physical considerations Therefore, the SM has been applied to ions in region I only. A simple shell model (SSM) as well as a deformable shell model (DSM), as proposed by Basu & Sengupta (1968), has also been used The semi-empirical DSM effectively introduces a three-body interaction and in that respect, has a little semblance of the Breathing Shell Model (Schroder 1966, Nusslein & Schroder 1967, Cochran 1971) However, the DSM offers greater manoeuverability because of being representable in the form of a central local potential (Sarker & Sengupta 1969)

2. Method of Calculation

The formation energy of Schottky defects, E_{SD}, is given by

$$E_{SD} = E_v^+ + E_v^- - E_s, \qquad \ldots (1)$$

where $E_v^{\pm}$ are the energies needed to extract a positive and a negative ion from the lattice, and

$$E_s = -\tfrac{1}{2} \sum_{\substack{l'\\ k'}}{}' \phi(r^{ll'}_{kk'}), \qquad \ldots (2)$$

ϕ is the interaction energy per ion pair, and E_s is the sublimation energy per ion pair. In fact, $E_v^{\pm}$ are the average energies of a lattice site (where the vacancy is thought to occur) before and after relaxation That is,

$$E_v^{\pm} = -\sum_{lk} \phi(|r^l{}_k + \eta\{r^l{}_k\}|) + \tfrac{1}{2} \sum_{\substack{ll'\\ kk'}} {}' [\phi(|r^{l'}{}_{k'} + \eta\{r^{l'}{}_{k'}\}| - |r^l{}_k + \eta\{r^l{}_k\}|) - \phi(|r^{l'}{}_{k'} - r^l{}_k|), \qquad \ldots (3)$$

where η indicates the displacement. The relaxation is caused by the creation of a vacancy and the relaxed configuration of the lattice is calculated in the following way.

The six immediate neighbours of the vacancy are thought to form a region I and the rest of the lattice forms a region II. The displacements of the ions in region I, ξ (in unit of r_0), is found out by an exact lattice calculation through the force-balance procedure (ML) Since results of the continuum theory are applied to region II, we have to postulate two different origins for the displacement of ions in that region—(i) the polarization of the lattice by the field of the unbalanced charge at the vacant lattice site (electric part), (ii) the relaxation of the nearest neighbours causing a general relaxation of all ions (elastic part). The pertinent equations for finding our these displacements are given, for example, in Bassani & Fumi (1954) and Chaudhuri *et al* (1973) In these calculations, we have used an elastic strength given by BL, namely,

$$k = \xi - M', \tag{4}$$

where M' has been defined by ML

In finding out the relaxation of the nearest-neighbour ions and later in the calculation of the energy of the lattice site where the vacancy occurs, we have postuloted the following interactions between the ions

(i) Coulomb interaction,

(ii) repulsive interaction of the form,

$$\phi_{kk'}^{ll'}(r_{kk'}^{ll'}) = \beta_{kk'}\, b \exp[(r_k + r_{k'} - r_{kk'}^{ll'})/\rho_{kk'}] \qquad \ldots \quad (5)$$

extended upto next nearest neighbours,

(iii) van der Waals interaction, as,

$$\Psi_{kk'}^{ll'}(r_{kk'}^{ll'}) = -c_{kk'}/(r_{kk'}^{ll'})^6 - d_{kk'}/(r_{kk'}^{ll'})^8. \qquad \ldots \quad (6)$$

and,

(iv) a local central three-body interaction given by

$$\chi = \sum_{\substack{lk \\ cnn}} \sum_{\substack{l'l'' \\ k''k''}} A(k) \exp|-\{r_{kk'}^{ll'} + r_{kk''}^{ll''}\}/\rho_{kk'}|, \qquad \ldots \quad (7)$$

where k-th ion is the common nearest neighbour of the ions k' and k''. Two sets of calculations were performed with and-without the fourth term.

Detailed expressions for use either in the force-balance procedure or in the relaxation energy calculation have been given by Chaudhuri *et al* (1973) and in the references cited therein These expressions are derived on the basis of a point polarizable ion model (PPIM) For the SM and DSM, the equations for the force blance of region I will contain explicitly the displacements of the shell and core of the ions and different sets of equations have to be solved simultaneously to find out the shell and core displacements. The Coulomb part of the forces,

$c_j^{\beta}(+)$ is given by the equation (in units of e^2/r_0^2, e is the electronic charge and r_0 is the hormonic interionic separation),

$$c_j^{\beta}(+) = \sum_{\alpha} \sum_{k}^{I\prime} Y_j^{\beta} Y_k^{\alpha} \left| 1/(r_{jk}^{\beta\alpha})^2 - 1/(s_{jk}^{\beta\alpha})^2 \right| \; i - n \; M_+' - n_- M_-'$$

$$+ (n_+ - n_-)k - Ke^2(\xi_j^{\beta} - \xi_j^{\alpha})/r_0 \qquad (8)$$

run from 1 to 2 (1 = core, 2 = shell)

$$\mathbf{r}_{jk}^{\beta\alpha} = \mathbf{t}_{jk} + \boldsymbol{\xi}_j^{\beta} + \boldsymbol{\xi}_k^{\alpha} \qquad \ldots \quad (9)$$

$$S_{jk} = \mathbf{t}_{jk} + \boldsymbol{\xi}_k^{\alpha} \qquad \ldots \quad (10)$$

Here Y's are shell and core charges and K is the core-shell spring constant. I in the summation indicates that it has to be performed over the ions in the region I. $M'_{\pm}$ are electronic plus displacement dipole moments of ions in the region II. $\mathbf{t}_{jk}$ is the distance (in units of r_0) from the site j to the site k in the unrelaxed lattice and ξ's are relaxations of ions around the defect. n_j (j = + or −) are lattice summations of the type

$$n_j = \sum_{l}'(t_{vl}\, t^{\wedge}_{lj})/(t^2_{vl} t^3_{lj}), \qquad \ldots \quad (11)$$

where the subscript v indicates the vacancy site and l runs over all + ions for j = + and so on. These summations have been evaluated by ML.

The repulsive force originating from the overlap of the electron cloud was considered in the shell force balance, while the van der Waals type forces originating from the multiple expansion of the charge cloud of ions were assumed to be centered around the core of the ions. As an alternative procedure, we could have assumed to have the expansion occur around shells of ions. However, the effect of the van der Waals forces is, in general, not pronounced in the case of alkali halides (Stoneham & Batram 1970) and therefore we did not try the alternative. The three-body type force, when considered, was assumed to influence the shell force balance. A consistent procedure was adopted in finding out the relaxation part of $E_v^{\wedge}\pm$.

3. Results and Discussion

The input data for the calculations have been listed in table 1 with the references cited therein. Van der Waals coefficients are those of Mayer (1933) and ionic polarizabilities were taken from Tessman *et al* (1953). Tor (1964) ionic radii were used. Parameters for the repulsive and three-body interactions were calculated utilising the equilibrium condition, values of harmonic differences of elastic constants, ($\tilde{C}_{12}$-$\tilde{C}_{44}$), and bulk moduli of crystals. Very recently Boswarva & Simpson (1973) have found that Born-Mayer repulsive parameters obtained from *dielectric data* showed better agreement with experimental E_{SD} values than those obtained from the *elasticity data*. We believe, their parameters were derived

from the room temperature elasticity data. Ours, however, have been figured out from the harmonic ($T = 0°K$) elasticity data. The coefficient for the three-body interaction could be split into two parts, corresponding to two types of ions, from a fit between the theoretically derived expression and the experimentally observed phonon frequency at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ (Chaudhuri *et al* 1973 for details). The SM parameters for a negative ion polarizable model were determined following the procedure outlined by Woods *et al* (1960). All these parameters are listed in table 2.

Values of dipole moments and fractional displacements of nearest neighbour for the PPIM, and fractional core and shell displacements of the SM are not given here. They will be available on request. For the PPIM, the problem of finding out these displacements amounts to finding a solution of the equation $f(\xi) = 0$, where $f(\xi)$ is some function of ξ. This problem could be solved to an error value of 1×10^{-6} in an IBM 1130 computer by utilizing a subroutine which combined interval bisection and rational fraction interpolation. For the SM, two simultaneous equations of the nature

$$f(\xi_c, \xi_s) = 0,$$

and

$$g(\xi_c, \xi_s) = 0,$$

Table 1 Input data for different crystals. References in column 5 pertain to r_0, $(\tilde{C}_{12}\text{-}\tilde{C}_{44})$ and β values

Crystal	r^0 Å	$(\tilde{C}_{12}-\tilde{C}_{44})$ $\times 10^{-12}$ dynes/cm^2	Compressibility $\beta \times 10^{12}$ cm^2/dyne	Ref	c_0^s	c_∞^s	$\omega \times 10$ rad sec
NaCl	2 79	−0 031	3.614	a	5 90	2.25	4 33[h]
NaBr	2 951	−0.013	4.348	b	6.40	2.60	3 599[i]
NaI	3.198	−0 002	5.504	c	6.60	2 91	3 236[j]
KF	2.637	−0 001	2.772	d	5 50	1.50	5 35[k]
KCl	3.108	−0.012	4.785	a	4.85	2.10	3 05[l]
KBr	3.258	−0.004	5 577	e	4.90	2.30	2.695[m]
KI	3.484	−0.013	7.559	f	5.10	2 70	2 476[n]
RbCl	3 239	0.026	4 902	g	4.90	2 20	2.62[o]
RbBr	3.408	0.003	6 154	b	4.90	2.30	1 83[p]
RbI	3 625	0 007	7.519	b	5.50	2 60	1 62[q]

a. Leibfried & Ludwig (1961)
b Lewis *et al* (1967)
c. Claytor & Marshall (1960)
d Marshall & Miller (1967)
e. Nikanorov & Stepanov (1960)
f Nusslein & Schroder (1967)
g. Marshall *et al* (1967)
h. Raunio *et al* (1969)
i Reid *et al* (1970)
j. Woods *et al* (1960)
k. Buhrer (1970)
l Raunio & Almqvist (1969).
m. Woods *et al* (1963)
n. Dolling *et al* (1966)
0 Raunio & Rolandson (1970a)
p. Rolandson & Raunio (1971)
q. Raunio & Rolandson (1970b)
s. Burstein (1964).

Table 2. Calculated parameters for different crystals

Crystal	Without threebody			
	ρ(Å)	($10b^{-12}$ erg)	y	$K \times 10^{-12}$ dynes/cm
NaCl	0.3170	0.2592	2 0897	28 0491
NaBr	0 3304	0 2338	2 2311	23.1643
NaI	0.3445	0 2034	2 3652	18 2061
KF	0.2946	0.2727	2.7911	138.222
KCl	0.3152	0 2353	3 4986	69 2402
KBr	0.3235	0.2153	3.5159	53 3713
KI	0 3600	0 2084	2.5940	18 3549
RbCl	0 3005	0 2055	6 4510	202 70
RbBr	0.3218	0.2064	5.1140	101 911
RbI	0 3339	0.1857	6 4463	117.972

Crystal	with three body					
	ρ(Å)	($10b^{-12}$ erg)	y	$K \times 10^{-12}$ dynes/cm	$A(1) \times 10^{4}$ ergs	$A(2) \times 10^{4}$ ergs
NaCl	0.2963	0 2606	3.2818	76 5431	0.011	−0 0167
NaBr	0.3193	0.2348	2 6993	35 4152	0.0176	−0 0197
NaI	0 3422	0.2037	2 4435	19.600	0 0191	−0 0196
KF	0.2941	0.2728	2 8697	146.405	0 0096	−0.0103
KCl	0.3044	0.2353	4.5212	118 187	0 0730	−0 0851
KBr	0.3191	0.2153	3 8231	63.702	0.0752	−0.0801
KI	0 3399	0.2083	3 8902	33.117	0 0512	−0 0722
RbCl	0.3259	0.2046	3 5332	58 275	0 0954	−0.0702
RbBr	0 3255	0.2065	4 7390	87 0493	0 1136	−0.1069
RbI	0 3449	0 1857	5 2168	76.317	0.1221	−0.1017

where f and g are two different functions of ξ_c and ξ_s, had to be solved. For that purpose we utilized the same subroutine and found out two sets of ξ_s (corresponding to two equations) for several selected values of ξ_c, and then graphically found out ξ_s and ξ_c values which satisfy both the equations A representative plot for one of the crystals has been shown in figure 1 However, this procedure of finding out ξ_s and ξ_c failed for RbI, because the two curves did not intersect at all. An adjustment of H and K values might have brought them closer and, possibly made them intersect But we did not try that (see later)

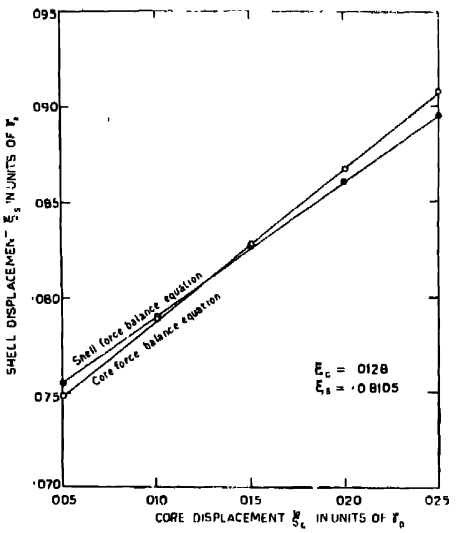

Fig. 1. A representative plot for one of the crystals (NaBr) necessary to determine ξ_C and ξ_S

Table 3. Energy of formation of Schottky defects for different crystals

Crystals	Without three body			
	$E_v^1(P.P.I.M)$ / $E_v^1(S.M.)$ e.v.	E_v-e.v.	$E_{SD}(P.P.I.M)$ / $E_{SD}(S.M.)$ e.v.	% Dovn. from expt.
NaCl	4.8306 4.8762	5 4730	2.2036 2.2492	−3 5623 −1 5666
NaBr	4 4562 4 1475	5 1961	1.9617 1 6536	+ 5 4674 −11 0970
NaI	4.0124 3 5140	4 8801	1.7313 1.2329	−23.7310 −45 6870
KF	5.5836 5 3253	5 6252	2.5941 2.3358	− 1.7386 −11.5240
KCl	4.7203 3 9952	5.0755	2 3905 1.6654	+ 5.7740 −26 31
KBr	4 4313 3.4622	4.9068	2.2471 1 2780	+ 3.5529 −41.1050
KI	3.9691 3.1759	4 5825	1 9402 1 1469	+ 22 7970 −27.4110
RbCl	4 7195 3.5597	4.9301	2.4320 1.2722	+21.60 −36 39
RbBr	4.1472 3.3611	4 6996	2 0015 1.2154	
RbI	3.9888 4 9805	4.4939	2.0140 3.0056	

Table 3 (contd.)

Crystals	with three body				Experimental value in e.v.
	E_v+(P.P.I.M) / E_v'(S.M.) e.v.	E_v− e.v.	E_{SD}(P P I M) / E_{SD}(S M) e.v.	% Devn. from expt.	
NaCl	4 8032 4 4169	5 6390	2 3059 1.9197	+ 0.9110 − 1.5987	2 285 +0 17a,b
NaBr	4 3381 3.8481	5 3939	2 0216 1 5346	+ 8 8197 −17.4940	1 86 + 0.27c,d,e
NaI	3.8952 3 4183	5 0129	1 7442 1 2673	−23 1630 −41 1720	2.27 f
KF	5 4696 5 2218	5 7862	2 6403 2 3926	+ 0 11361 + 9 3717	2 64 g
KCl	4 6654 3 7370	5 2068	2 4502 1 5217	+ 8.4158 −32.6690	2 26 +0 01 b, h
KBr	4.3596 3.3034	5.0152	2.2776 1 2215	+ 4 9583 − 43 7110	2.17 +0.25 i,j,k
KI	3 9369 2 9533	4 7063	2 0058 1 0222	+26 9490 −35 3040	1 58 +0 02 l,m
RbCl	4 5153 3 2806	5.0581	2 3900 1 1553	+ 19.50 −42 235	2 0 n
RbBr	4 0726 3.1982	4 7700	2 0025 1 1282		
RbI	3 9068 4.8070	4 5458	1 9965 2 8967		

a. Allnatt *et al* (1971)
b. Dreyfus & Nowick (1962)
c Schamp & Katz (1954).
d Phipps *et al* (1929)
e Barr (1971)
f. Hoodless *et al* (1971).
g. Suptitz & Teltow (1967).
h. Allnatt & Jacobs (1962).
i Rolfe (1964)
j Jacobs & Tomkins (1952)
k Phipps & Patridge (1929)
l Ecklu *et al* (1964)
m Jain & Parashar (1969)
n. Sastry & Muhmam (1969)

In table 3 two sets of calculated Schottky defect formation energies, E_{SD}, are shown. In this table the first set includes van der Waals forces while the second set includes both van der Waals and three-body forces. Corresponding to each set, two values of E_{SD} appear—one due to the PPIM and the other due to the SM. Experimental values of E_{SD} have been presented in a different column and comparison has been made between the experiment and the theory wherever possible. In some of the experimental values error estimates have been indicated

These are, in fact, standard deviations around the mean of different experimental values. Table 3 also records energies of extractions of isolated positive and negative ions, $E_v^{\pm}$, from the lattice

It can also be noted that the three-body forces do not have any significant effect on the E_{SD} values. In order for searching an alternative polarization mechanism of the nearest neighbours, we have also calculated E_{SD}'s on the basis of an SM and the results are given in table 3.

However, it can be seen from table 3 that E_{SD} values calculated according to the PPIM have a better accord with the experiment then those obtained through the SM The reason might be that in the PPIM, the dipole moment of the nearest neighbours is taken as a parameter and is evaluated self-consistently from the force balance condition and from the general relation

$$\alpha_{\pm} F_e = \nu_{\pm} e$$

whereas in the SM the corresponding dipole moment is given by $Y_e(\xi_s - \xi_c) r_0$ This Y is found out from different sets of equations which are derived assuming certain types of interactions between the ions. Thus, the two procedures should approach to reproduce the same sets of values, as the assumed interactions between ions would approach to describe the reality. Another factor which might give rise to discrepancies between the theory and the experiment, may be uncertainties associated with the input data for the determination of L and K This point was examined and we found that the order of variation between different sets of dielectric data for a particular crystal at a fixed temperature is round 10%. For example, our input data of ϵ_0 for NaI is 6 60 and that of Lowdes & Martin (1969) is 7.31. This variation of $\pm 10\%$ (although a $\pm 5\%$ variation would be legitimate) of ϵ_0 and ϵ_∞ data for KCl around their given values in table 1 resulted in a large variation in Y and B, and a consequent variation in E_{SD}, so much so that in one case E_{SD} changed its sign In the same situation the PPIM did not exhibit more variation than that had been introduced The results of the pertinent calculations have been displayed in table 4

The above discussion indicates that for a small variation of input parameters there is a considerable change in E_{SD} when and SM is used for the calculation A number of different sets of parameters appear in the literature which do not always agree well and there are no simple criteria for choosing between the various sets

From the results displayed in table 4, it seems that a criterion has been found out for fixing Y and K values The criterion is the following : choose Y and K for a system from a multitude of possible values such that they can reproduce the PPIM predictions of E_{SD} or the experimental E_{SD} if available. It needs be mentioned here that although the SM has some theoretical basis (Sinha 1968,

Table 4. Two extreme sets of shell model parameters (obtained by adjusting the value of dielectric constants within their experimental uncertainties, the ad-hoc variations of ϵ_0 and ϵ_∞ having been indicated in paranthesis) and corresponding energy of formation of Schottky defects in KCl

Crystal	ϵ_0	ϵ_S	Without three body			With three body		
			γ	$K\times10^{-12}$ dynes/cm	$E_S(P.P.I.M)$ / $E_S(S.M.)$ ev	γ	$K\times10^{-12}$ dynes/cm	$E_S(P.P.I.M)$ / $E_S(S.M.)$ ev
KCl	4.36 (−10%)	2 31 (+10%)	2 3382	24 7688	2 6126 / 2 0826	2.7915	36 8365	2.6852 / 2 0126
	5.34 (+10%)	1.89 (−10%)	6 7960	320 6969	2 3624 / 1 5095	11 7156	961 0344	2.4468 / −0 1442

1969) the values of the parameters of the model are ambiguous For example although Ye has been defined as the shell charge, the values reported in the literature seem to be arbitrary In other words, the values of Ye has no correlation to the free ion shell charge which is normally expected No successful correlation has yet been established for a systematic variation of Y and K for different crystals. The reason may be that no property has been explored in which some experimental quantity is sensitive to the variation of Y and K We have, however, found that E_{SD}'s are rather sensitive to this variation It is hoped that they can be utilized to find out Y and K and it will be interesting to see if such Y's and K's of different crystals can give rise to a correlation among themselves

Acknowledgment

We thank Professors A K Barua and S Sengupta for their interest and encouragement. One of us (A K G) thanks the Council of Scientific & Industrial Research, New Delhi, for financial support

References

Allnatt A. R & Jacobs P. W 1962 *Trans. Faraday Soc.* **58**, 116
Allnatt A. R , Pantelis P. & Sime S J 1971, *J. Phys. C* **4**, 1778.
Barr L. W. 1970 *unpublished results referred to* by Hoodless *et al* (1971)
Bassani F. & Fumi F. G. 1954 *Nuovo Cimento* **11**, 274
Basu A. N. & Sengupta 1968 *Phys Stat. Solidi.* **29**, 367
Boswarva I. M. & Lidiard A B 1967 *Phil Mag* **16**. 805
Boswarva I. M. & Simpson J H. 1973 *Canad J Phys.***51**, 1923
Brauer P. 1952*E Naturforsch* **7a**, 372.
Buhrer W. 1970 *Phys Stat. Solidi* **41**, 789.
Burstein E, 1964*Phonon and phonon interaction* (Ed. T. A. Bak, Benjamin, N.Y) p 206.

Chaudhuri S, Sen S. & Roy D. 1973 *Phys Stat Solidi* (b), **56**, 403.
A(1) and A(2) values in table 2 of this reference have been inverted through final results and are free from this error
Claytor R N & Marshall B. J 1960 *Phys Rev* **120**, 332.
Cochran W 1971 *Crit. Rev Stat State* **2**, 1.
Dick B. G. & Overhauser A. W 1958 *Phys. Rev.* **112**, 90.
Dolling G, Cowley R A, Schittenhelm C & Thorson I M, 1966 *Phys. Rev* **147**, 577.
Dreyfus R W & Nowick A. S 1962 *J. Appl Phys Suppl*, **33**, 473.
Ecklin D, Nadler C & Rossel J 1964 *Helv. Phys Acta* **37**, 692.
Hardy J R. & Lidiard A. B. 1967 *Phil. Mag.* **15**, 825
Holt J. B, Socke H G & Schmalzried H 1969 *J. Am. Ceram. Soc* **52**, 376
Hoodless I. M, Strange J M. & Wylde L. E, 1971, **4**, 2737
Jacobs, P. W M. & Tomkins F C 1952 *Quart. Rev Chem. Soc.* **6**, 238
Jain, S. C & Parushar D. C 1969 *J. Phys* **C2**, 167
Kanzaki H 1957 *J Phys. Chem Solids* **2**, 24.
Karo A M. & Hardy J. R. 1971 *Phys. Rev* **133**, 3418.
Kurosawa T 1958 *J Phys Soc Japan*, **13**, 153.
Leibfried G & Ludwig W. 1961 *Solid State Phys* (Eds. Seitz F, and Turnbull D, Academic Press, N Y) 12, 275.
Lewis J. T., Lehoczky A & Briscoe C V 1967 *Phys Rev.* **161**, 877
Lowndes R P. & Martin D. H 1969 *Proc Roy Soc* (*London*) **A308**, 473.
Margenau H. 1939 *Rev Mod Phys* **11**, 1.
Marshall B J. & Miller R. E 1967 *J Appl Phys.* **38**, 4749
Marshall B. J, Pealerson D O & Dorris G G 1967 *J. Phys Chem Solids*, **28**, 1061
Mayer J E 1933 *J Chem. Phys.* **1**, 270, 327
Mott N F & Littleton M J. 1938 *Trans Faraday Soc* **34**, 485.
Nikanorov S. P & Stepanov A. V 1960 *Sov. Phys. JETP*, **10**, 1280
Nusslein V. & Schroder U 1967 *Phys Stat. Solidi*, **21**, 309
Phipps T E. & Patridge E. G 1929 *J Am. Chem Soc* **51**, 1331
Rauml G & Almqvist L. 1969 *Phys Stat. Solidi* **33**, 209
Raunio G, Almqvist L & Stedman R. 1969 *Phys Rev*, **178**, 1496.
Raunio G & Rolandson S 1970a *J. Phys* **C3**, 1013
Raunio G. & RolandsonS 1970b *Phys. Stat Solidi* **40**, 749
Reid J. S, Smith T. & Buyers W J L. 1970 *Phys Rev.* **B1**, 1833
Rolandson S. & Raunio G. 1971 *J. Phys* **C4**, 958
Rolfe J 1964 *Canad J. Phys* **42**, 2195
Sarkar A K. & Sengupta S 1969 *Sol. State Comm* **7**, 135
Sastry P. V. & Mukhnam B. G 1969 *Phil Mag* **20**, 859
Schamp H W & Katz E. 1954 *Phys Rev* **94**, 828
Schalz A H. 1968 *Phys Stat. Solidi*. 25, 285.
Schroder U 1966 *Sol. State Commun.* **4**, 347
Sinha S K 1968 *Phys. Rev.* **169**, 477
Sinha S K 1969 *Phys. Rev* **177**, 1256.
Stoneham A. M & Batram R. H. 1970 *Phys. Rec.* **B2**, 3403
Suptiz P & Teltow J. 1967 *Phys. Stat Solidi* **23** 9.
Tessman J R Kahn A. H. & Shockley W. 1953 *Phys Rev.* 92, 890
Tosi M P. 1964 *Solid State Physics* (Eds Seitz F. and Turnbull D Academic Press, N.Y), 16,1.
Woods A D. B, Cochram W & Brockhouse B N 1960 *Phys Rev.* **119**, 980
Woods A D. B, Brockhouse B. N. & Cowley R. A. 1963 *Phys. Rev* **131** 1025.